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INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification [6] :
E21B 37/06

A1

(11) International Publication Number: WO 96/37683

(43) International Publication Date: 28 November 1996 (28.11.96)

(21) International Application Number: PCT/GB96/01238

(22) International Filing Date: 23 May 1996 (23.05.96)

(30) Priority Data:
9510563.1 24 May 1995 (24.05.95) GB

(71) Applicant *(for all designated States except US)*: AEA TECHNOLOGY PLC [GB/GB]; 329 Harwell, Didcot, Oxfordshire OX11 0RA (GB).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: BOURNE, Hugh, Malcolm [GB/GB]; 1 Turnberry Drive, Inverurie, Aberdeenshire AB51 3WT (GB). LAWLESS, Thomas, Anthony [GB/GB]; 46 Overcombe Drive, Preston, Weymouth, Dorset DT3 6QF (GB). SMITH, Roger, Neal [GB/GB]; 17 Meadowview Road, Weymouth, Dorset DT3 5PB (GB).

(74) Agent: MANSFIELD, Peter, Turquand; AEA Technology plc, Patents Dept., 329 Harwell, Didcot, Oxfordshire OX11 0RA (GB).

(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

Published
With international search report.
Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: WELL INHIBITION

(57) Abstract

Deleterious processes such as scale deposition in an oil well extending through a formation are inhibited by injecting an emulsion into the formation. The emulsion contains an aqueous solution of an inhibitor as a dispersed phase in an oil phase such as kerosene. The emulsion is arranged to break down when injected into the formation, for example by an appropriate choice of surfactant, so the inhibitor is adsorbed or precipitated in the formation. The use of the emulsion can be advantageous in wells with poor pressure support, and in formations susceptible to deconsolidation by acids.

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Well Inhibition

This invention relates to a method of inhibiting deleterious processes in a well such as an oil well, particularly but not exclusively for inhibiting scale deposition.

It is known to supply inhibiting chemicals to oil wells (and gas wells) to suppress processes such as corrosion, scale deposition, or emulsification which might otherwise occur. Such inhibitors may be supplied in the form of solutions in either water or in an oil-like liquid such as kerosene. A wide variety of scale inhibitors are known; and scale inhibitors may be injected or squeezed into the rock formation surrounding a well, so that the inhibitor chemicals are gradually released into the produced fluids over a period, possibly of several months. The inhibitor in some cases is adsorbed by the formation, while with other formulations it is precipitated. For example US 4 947 934 (Hen; Mobil Oil) describes a method of scale inhibition in which an acidic aqueous solution containing polyacrylate inhibitor and a polyvalent cation are injected into the formation. EP 0 371 667 A (Conoco) describes the injection of an aqueous solution of a phosphonate inhibitor and a metal chelate, the chelate having a lower stability constant than the inhibitor, so precipitation of the metal phosphate occurs in the formation. GB 2 250 738A (Marathon Oil) describes the use, in a squeeze treatment to inhibit scale, of an aqueous solution of a polyvinyl sulphonate of molecular weight above 9000. EP 0 030 425 A (Cyanamid) describes the use, in a squeeze treatment, of an emulsion comprising a water-soluble polymeric antiprecipitant dispersed in an oil phase, with at least two surfactants which ensure that the emulsion inverts or

breaks on contact with water, to release the antiprecipitants.

According to the present invention there is provided a method of inhibiting deleterious processes in a well extending through a formation, the method comprising injecting into the formation an emulsion containing an aqueous solution of an inhibitor or an inhibitor component as a dispersed phase in an oil phase, the emulsion being such that the phases separate after injection into the formation, due to inherent properties of the emulsion and the temperature and/or time and/or mechanical stresses to which it is subjected.

The breakdown of the emulsion and consequent separation of the phases may occur as a result of a change of temperature, or simply as a result of the time which has elapsed whilst resident in the formation. The breakdown thus does not depend upon the nature of the other fluids encountered by the emulsion within the formation. As the emulsion breaks down the inhibitor is adsorbed or precipitated onto the formation.

It will be appreciated that the aqueous solution may include liquids other than water, for example alcohols, as long as they are not soluble in the oil phase; and that additional materials other than the inhibitor may be dissolved in it. The term "oil phase" means a relatively non-polar substance which is not soluble in the aqueous solution, and which is miscible with any crude oil produced from the formation. A suitable oil phase is kerosene.

In general a separate surfactant or emulsifying agent will also be required to form the emulsion, which is preferably a non-ionic emulsifier as such emulsifiers -

tend to tolerate changes in salinity while being sensitive to temperature. The emulsifier must have a hydrophilic/lipophilic balance (HLB) suited to the other liquids present in the emulsion, and an HLB value less than 8 is generally desirable for forming such a water-in-oil ('invert') emulsion. Examples of emulsifiers which may be suitable are alkoxylated amines, glycols or substituted phenols, ethoxylates, or sulphonates. Indeed the emulsion may contain more than one emulsifier.

The invention provides particular benefit when used in a low flow oil well, where the pressure causing oil to flow into the well may be insufficient to displace water from the formation if the well is subjected to a conventional squeeze with an aqueous inhibitor solution. It also is beneficial in wells where the formation is calcite-cemented sandstone, as many conventional aqueous inhibitors are acidic and so cause extensive deconsolidation of the formation.

In a modification, the oil phase is itself a dispersed phase within a continuous external aqueous phase: thus the emulsion is a water-in-oil-in-water emulsion. In this case the two aqueous phases (the dispersed aqueous phase and the continuous aqueous phase) may contain different inhibitor components which react when the emulsion breaks down. For example the dispersed aqueous phase may contain a phosphonate, or a polycarboxylic acid or a polyacrylic acid (e.g. phosphinopolycarboxylic acid, or diethylenetriaminepenta-(methylenephosphonic acid), as described in US 5 090 479 (Read/Statoil)), and the continuous aqueous phase contain a dissolved calcium salt such as $CaCl_2$. The use of such a three-phase emulsion provides the same benefit mentioned

above in formations susceptible to deconsolidation by acids.

Thus the concept of the invention is to inject into the formation an invert emulsion with an inhibitor such as a scale inhibitor in the dispersed, aqueous phase. At a defined temperature/time (appropriate to field conditions) the emulsion resolves to release the aqueous inhibitor into contact with surfaces of pores in the formation, so the inhibitor is retained on those surfaces, whilst the oleic phase remains in continuity with oil in adjacent pores so that subsequent flow of oil through the formation is not suppressed.

The invention will now be further and more particularly described, by way of example only. One example is in providing scale inhibitor into an oil well which has poor pressure support, and so low oil flow, so that it is preferable to maintain oil phase continuity through the pores of the formation. The scale inhibitor in this particular example is sodium polyacrylate containing a phosphorus label (Bevaloid IP-12B; trade mark) as a 2% aqueous solution; this is mixed with an oil phase such as kerosene and a suitable surfactant, and blended at high speed (for example with a Silverson blender; trade mark) so as to form an invert emulsion. The invert emulsion is then injected into the formation, where it breaks down to allow the inhibitor to be retained. The oil well can then come back on stream again rapidly, as an oil phase is still present in the pores of the formation.

It will be appreciated that the physical parameters such as temperatures in the region of the formation into which injection is to be performed will be different for different wells, and so the invert emulsion has to be

suited to that well. For example in one well it may be desirable for the emulsion to break down at 115°C, while in another well the break-down temperature (i.e. the temperature in the formation where break down is to occur) might be 130°C or 75°C. It may also be necessary for the emulsion to remain in the formation (and so at elevated temperature) for a prolonged time such as 1 hour or 6 hours, before it breaks down. Furthermore the emulsion should be stable in contact with oil field liquids such as oil or brine; it should have a viscosity similar to or greater than that of the oil in the well, and it is preferably not affected by any shear effects experienced during injection. It is thus clear that the emulsion, and in particular the surfactant, must be selected and formulated to suit a particular well.

Surfactants can readily be selected for this use, as they should generally have an HLB value less than 8 in order to stabilise an invert emulsion, more preferably between 3 and 6. It will be appreciated that a mixture of different surfactants, differing in their HLB values, may be used. Another criterion which can sometimes provide guidance is the cloud point of the surfactant, that is the temperature at which an aqueous solution of the surfactant becomes cloudy as the surfactant comes out of solution; the cloud point temperature provides an indication of the temperature at which the emulsion can be expected to break.

For example a suitable emulsion might use as the continuous (oil) phase kerosene, or a mixture of kerosene with oil, or a long chain alcohol (e.g. C_{10}), or esters, which are compatible with the oil from the well. As discussed earlier the aqueous phase contains the scale inhibitor; it might be seawater or demineralised water,

and should be of suitable pH to maximise inhibitor retention in the formation. The surfactant might for example be a mixture of 2 parts sorbitan trioleate (with HLB = 1.8) to 15 parts sorbitan mono-oleate (with HLB = 4.3), so the resultant HLB is about 4.0. These surfactants are available for example from Croda Chemicals, Goole, England and are widely used as industrial water-in-oil emulsifiers. Other surfactants which might be used are glycerol mono-oleate (HLB = 3.4), glycerol monostearate (HLB = 3.8), or glycerol monolaurate (HLB = 5.2). Alternatively the surfactant might be a non-ionic block copolymer, such as a copolymer of polyhydroxy fatty acid and polyalkyleneglycol; such a copolymer is Hypermer B246 or Hypermer B239 (trade marks), and has an HLB value of about 6.0. Such surfactants tend to be substantially insoluble in water, so the emulsion is made by dissolving the surfactant in the selected oil phase, before mixing vigorously with the aqueous phase.

The quantity of surfactant is preferably between about 1% and 5% by weight, for example between 2% and 3%. This can be expected to provide some excess surfactant, in the event that there is some adsorption of surfactant by rock surfaces. The quantity of the aqueous phase is preferably in the range 20% to 50% by weight, the remainder being the oil phase, so that the volume of the aqueous phase is less than that of the oil phase. The resulting emulsion desirably has a viscosity higher than that of the oil in the formation, though preferably not more than two hundred times, more preferably between 1.5 and 20 times the viscosity of the formation oil, for example about 2 or 10 times.

It will be appreciated that the selection of the components and their proportions must be chosen to suit a

particular well, taking into account the temperature in the formation, and the properties of the oil in that formation. It will be also appreciated that other types of surfactant may be used in place of or mixed with those discussed above, for example a high molecular-weight fatty amine blend (cationic, with HLB of about 4.5) or calcium stearoxyl-2-lactylate (anionic, with HLB of 5.1). Water-in-oil emulsions made with ionic surfactants such as these will tend to invert when the temperature is raised, although the emulsion can also be affected by the salt concentration. In any event as an emulsion is left in contact with rock surfaces there may be adsorption of surfactant onto those surfaces, and possibly also hydrolysis of surfactant, so that the critical monomer concentration in the oil phase is no longer exceeded (as is required for stability), so the emulsion breaks down.

Claims

1. A method of inhibiting deleterious processes in a well extending through a formation, the method comprising injecting into the formation an emulsion containing an aqueous solution of an inhibitor or an inhibitor component as a dispersed phase in an oil phase, the emulsion being such that the phases separate after injection into the formation, due to inherent properties of the emulsion and the temperature and/or time and/or mechanical stress to which it is subjected.

2. A method as claimed in Claim 1 wherein the phases of the emulsion separate as a result of a change of temperature.

3. A method as claimed in Claim 1 or Claim 2 wherein the oil phase is a dispersed phase within a continuous external aqueous phase.

4. An emulsion suitable for use in a method as claimed in any one of the preceding Claims.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 96/01238

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 E21B37/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 E21B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 030 425 (CYANAMID OF GREAT BRITAIN) 17 June 1981 cited in the application see the whole document	1-4
A	US,A,3 185 217 (BROOKS ET AL.) 25 May 1965 see column 3, line 62 - line 66	1-4
A	US,A,3 799 265 (WEBB) 26 March 1974 see the whole document	1-4
A	EP,A,0 447 120 (MOBIL OIL) 18 September 1991 see the whole document	1-4

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
12 September 1996	20.09.96

Name and mailing address of the ISA	Authorized officer
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Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	GB,A,2 244 073 (DEN NORSKE STATS OLJESELSKAP) 20 November 1991 cited in the application see the whole document	1

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Information on patent family members

International Application No
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